NITROGEN REMOVAL FROM LOW QUALITY NATURAL GAS

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INTRODUCTION

Natural gas provides more than one-fifth of all the primary energy used in the United States. It is especially important in the residential sector, where it supplies nearly half of all the energy consumed in U.S. homes. However, significant quantities of natural gas cannot be produced economically because its quality is too low to enter the pipeline transportation system without some type of processing, other than dehydration, to remove the undesired gas fraction. Such low-quality natural gas (LQNG) contains significant concentration or quantities of gas other than methane. These non-hydrocarbons are predominantly nitrogen, carbon dioxide, and hydrogen sulfide, but may also include other gaseous components. The nitrogen concentrations usually exceeds 4%.

Nitrogen rejection is presently an expensive operation which can present uneconomic scenarios in the potential development of natural gas fields containing high nitrogen concentrations. The most reliable and widely used process for nitrogen rejection from natural gas consists of liquefying the feed stream using temperatures in the order of -300°F and separating the nitrogen via fractionation. In order to reduce the gas temperature to this level, the gas is compressed, cooled by mullet-stream heat exchangers, and expanded to low pressure. Significant energy for compression and expensive materials of construction are required. Water and carbon dioxide concentrations must be reduced to levels required to prevent freezing.

SRI's proposed research involves screening new nitrogen selective absorbents and developing a more cost effective nitrogen removal process from natural gas using those compounds.

OBJECTIVE

The long-term objective of this project is to determine the technical and economical feasibility of a N_2 removal concept based on complexation of molecular N_2 with novel complexing agents. Successful development of a selective, reversible, and stable reagent with an appropriate combination of capacity and N_2 absorption/desorption characteristics will allow selective separation of N_2 from LQNG.

APPROACH

To achieve the objective we screened complexing agents in terms of their binding capacity and reversibility, conceptually designed a process flow diagram, and conducted an economic analysis of the process.

We established certain criteria for screening the nitrogen complexing agents. The desired properties for a successful complex are:

- It must be able to absorb/react with N_2 at the feed gas conditions of high pressure and it must be able to release N_2 at lower pressures for regeneration.

- The complex must bind and releases N_2 sufficiently and rapidly.

- The complex must be thermally stable and retain its ability to bind and release N_2 through pressure cycling.

- The complex must be stable in the presence of hydrocarbons, CO_2, H_2S, and O_2.

Consistent with the desired properties summarized above, we focused on a set of nonaqueous complexes. The complex we chose to study was tested at both low and high pressures.

PROJECT DESCRIPTION

The nitrogen absorbing ability of the nonaqueous complex was measured using two different gas absorption test apparatuses, one for low-pressure and the other for high-pressure absorption experiments. The methods of these experiments are described in the following sections.

Low Pressure Tests

Low-pressure (atmospheric) tests were conducted in the apparatus shown schematically in Figure 1. The test gases (N_2, CH_4 and/or Ar) were metered and blended using mass flow controllers. The Ar was used to set a baseline for absorption. The gas mixture was then directed to a bubbler that contained only a blank solvent (toluene) to saturate the gas mixture, and then the gas was sent to a bubbler containing the test solution. The emanating gases were then analyzed by a gas chromatograph (Hewlett-Packard 5890).

High Pressure Tests

High-pressure tests (up to 650 psia) were conducted on the complex using the apparatus shown schematically in Figure 2. The high pressure tests were conducted in a batch mode to avoid the excessively long dead-times that would appear in a flow mode (the amount of dead-space gas needed to be flushed is considerable at high pressures relative to the gas uptake by the test solution). Note that only one gas, either nitrogen or methane, may be tested at a time, although a second gas may be introduced after the first to measure mixed-gas uptake. The volume of the gas reservoir was measured to be 171.3 cm^3, and the remaining high-pressure volume (absorption vessel, valves, lines) was measured to be 297.5 cm^3. At the beginning of an absorption run, the chosen gas was sent through the entire system to purge out any gases previously occupying the apparatus. Next, the inlet and outlet valves to the absorption vessel were closed successively to allow the feed gas to pressurize the gas reservoir where it is pressurized. The pressure of the system was measured by a pressure transducer (Omega; Stamford, CT) placed between the gas reservoir and the absorption vessel.

After the gas reached the desired pressure, the inlet valve to the gas reservoir was closed. The inlet valve to the absorption vessel was opened next, allowing the gas in the reservoir to expand into the headspace above the liquid sample in the absorption vessel. The system pressure, recorded just after the expansion, then dropped as the feed gas was absorbed by the liquid sample. The pressure eventually reached equilibrium, which

depends on the gas's solubility in the test solution. Gas uptake in both blank solvent (toluene) and test solutions (nonaqueous complex) were measured, determining the extent to which nitrogen or methane binds to the complex.

RESULTS

Low Pressure Tests

Results for the low pressure tests are shown in Figure 3. It appears that competitive absorption is occurring within the complexing solution (Bhown et al., 1991), where the nitrogen is being desorbed by the methane. However, comparing a similar run with a blank sample (pure toluene present in the absorption bubbler) exhibits the same behavior. This indicates that neither the nitrogen nor the methane is binding with the complexing agent. The observed competitive absorption is due to the gases' comparative solubilities in the toluene. This is evidence of the complex not absorbing nitrogen at atmospheric pressures which meets part of the design criteria for a successful complex.

High Pressure Tests

A succession of gas absorption experiments were performed with 160 mL of a 56.5 mM complex solution. The results of these experiments are listed in Table 1. We measured a pressure drop, ΔP, of 115 psi when only methane was used as the feed gas. We also measured methane uptake in toluene (in the absence of complex), and we found the ΔP to be approximately 118 psi, close to that reported in the literature. Hence, we suspect that methane does not bind to the complex at high pressure.

Table 1

RESULTS OF THE ABSORPTION EXPERIMENTS WITH 160 mL OF THE 56.6 mM NONAQUEOUS COMPLEX

Feed Gas	Initial Pressure (psia)	Pressure Drop, P (psi)
Methane	597.7	115.0
Nitrogen	108.7	11.0
Nitrogen	177.7	4.0
Nitrogen	287.7	7.0

After releasing the methane from the absorption apparatus, three experiments using nitrogen as the feed gas were conducted in succession with the same solution. After one experimental run reached equilibrium, the apparatus was pressurized with more nitrogen and then allowed to reach a new equilibrium pressure. The results of the three experiments are shown in Table 1 and also in Figure 4. Figure 4 shows that complexation is indeed occurring (depicted by the hollow circles), but not to its full extent. However, this does demonstrate that the complex does not bind as readily with N_2 at lower pressures as it does with N_2 at higher pressures. This characteristic is beneficial because, in an actual natural gas process, the complex will be able to absorb N_2 at high partial pressures (200-400 psia) and then desorb it at low/atmospheric pressures. It should be noted that the complex

precipitates out of solution once it is bound to N_2. The complex redissolves in the solution once the N_2 is unbound.

Nitrogen absorption tests in the presence of methane were also performed with freshly made samples of the complex. The results are also plotted in Figure 4 (depicted by the solid square and circle) which indicates methane does not hinder the binding of the N_2 with the complex. This result shows that the complex is a good candidate for our application.

APPLICATION

Process Description

Figure 5 shows the process flow diagram for the commercial scale N_2-complexing absorption process. Natural gas is contacted with the complexing solution in a packed column. The lean solution exits the column consisting of toluene, unbound complex, and bound complex (in the form of a solid precipitate). The solution is then sent through a filtration process which collects the N_2-bound complex. Once collected, the pressure in the filter is lowered to release the N_2 and to regenerate the complex. The unbound complex is re-mixed with the lean solution and re-circulated to the rich feed tank.

Economics

The results of the economic analysis of this process are listed in Table 2. These are based on a dehydrated 20% N_2/80% CH_4 feed at 1000 psia. The capital and production costs using this process are $16.0 MM and $0.26/Mscf, respectively, for a 75 MMscfd plant. The capital and production costs for a 2 MMscfd plant are $1.7 MM and $1.22/Mscf, respectively. These values are compared to three other current N_2 removal technologies: cryogenic N_2 rejection, pressure swing adsorption, and lean oil absorption. From Table 2, we see that the production costs of the N_2-complexing absorption process compare well to the other technologies. Our process at 75 MMscfd is comparable or even more cost effective than the cryogenic process.

Table 2

COMPARISON OF COSTS BETWEEN SRI'S NITROGEN COMPLEXATION-BASED PROCESS AND OTHER CURRENT TECHNOLOGIES

Process	Gas Flow Rate (MMscfd)	Capital Cost ($MM)	Production Cost ($/Mscf)	Reference
SRI	2	1.7	1.22	
	75	16.0	0.26	
Cryogenic	2		1.00	Changela et al., 1991
	75		0.20-0.33	
Pressure Swing Adsorption	1		1.50-1.60	Echterhoff and Pathak, 1991
Lean Oil Absorption	1		3.00	Echterhoff and Pathak, 1991

FUTURE ACTIVITIES

Due to the promising results that we received form this study, we are continuing work in the second phase of this project.

During Phase II, we intend to design, construct, and operate a high pressure bench-scale unit capable of treating up to 0.25 Mscfd. This unit will differ from the earlier high pressure apparatus in that it will be a continuous absorption process as opposed to a batch configuration. We will vary key parameters such as gas and liquid flowrates, temperatures of operation (particularly desorption), gas pressure, and inlet nitrogen content. The resulting data will be useful for both demonstration and for obtaining scale-up parameters needed to design a commercial system. We will obtain other key information about the complex in Phase II, including its solubility (both unbound and bound to nitrogen) and its sensitivity to other components in natural gas. Using these data, we will conduct an economic evaluation of the process at commercial scales.

ACKNOWLEDGMENTS

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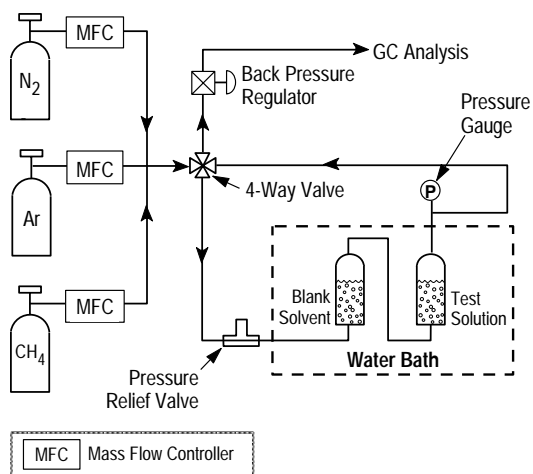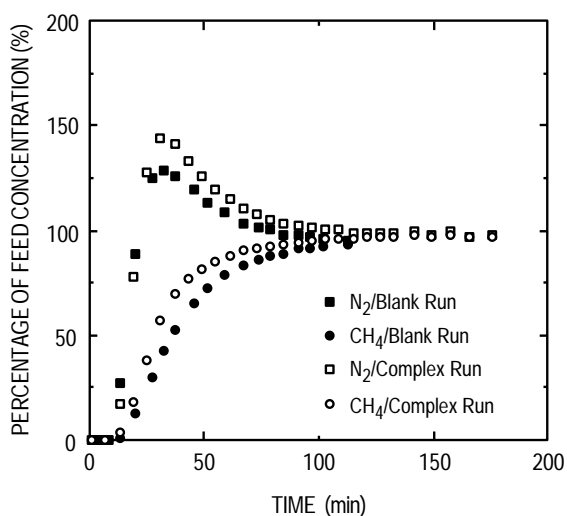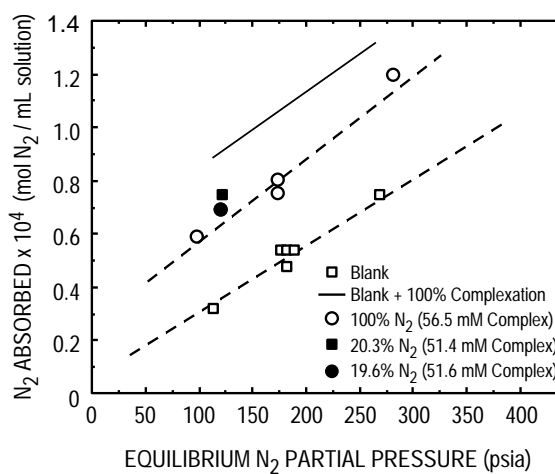
Figure 1. Low-pressure test apparatus.
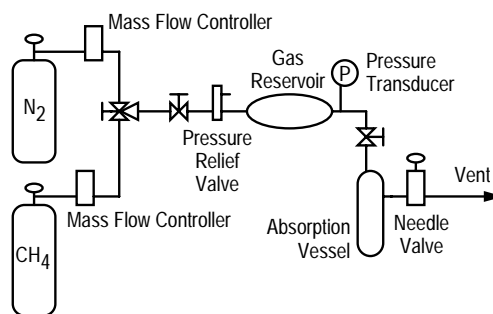
Figure 2. High-pressure test apparatus.

Figure 3. Comparison of blank 50% CH_4 / 50% N_2 experiments and the nonaqueous complex experiments.

Figure 4. High-pressure N_2 absorption in the presence and absence of CH_4 using the complex solution.